



**CERTIFICATION OF TRANSLATION**

I, Young-Ju Lee, an employee of Y.P.LEE, MOCK & PARTNERS of The Cheonghwa Bldg., 1571-18 Seocho-dong, Seocho-gu, Seoul, Republic of Korea, hereby declare under penalty of perjury that I understand the Korean language and the English language; that I am fully capable of translating from Korean to English and vice versa; and that, to the best of my knowledge and belief, the statements in the English language in the attached translation of the priority document (Korean Patent Application No. 00-25767), consisting of 16 pages, have the same meanings as the statements in the Korean language in the original document, a copy of which I have examined.

Signed this 21th day of Nov. 2003,

Youngju Lee

## ABSTRACT

[Abstract of the Disclosure]

5 A lithium secondary battery including an electrode assembly consisting of a cathode, an anode and a separator interposed between the cathode and the anode, a gel-state electrolyte solution consisting of a crosslinking product of prepolymer for forming epoxy resin and amine, a lithium salt and an organic solvent, and a case for accommodating the electrode assembly and the electrolyte solution. In the lithium secondary battery, swelling due to an electrolyte solution can be effectively suppressed  
10 and there is no concern about leakage of the electrolyte solution, so that the reliability and safety of the battery do not degrade.

[Representative Drawing]

FIG. 1

15

## SPECIFICATION

[Title of the Invention]

5

Lithium Secondary Battery

[Brief Description of the Drawings]

FIG. 1 is an exploded perspective view illustrating an exemplary general lithium  
10 ion battery; and

FIG. 2 is an exploded perspective view illustrating an exemplary general lithium  
ion polymer battery.

\* Explanation of Reference Numerals Designating the Major Elements of the  
15 Drawings

10, 21...electrode assembly                      11, 22...case

14, 14', 24, 24'...electrode terminal

[Detailed Description of the Invention]

20 [Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to a lithium battery, and more particularly, to a  
lithium battery having improved safety and reliability by using a gel-state electrolyte  
solution.

25 A lithium secondary battery generates electricity by lithium ions reciprocating  
between a cathode and an anode. The lithium secondary battery has a high energy  
density relative to the unit volume and voltage thereof compared to a Ni-Cd battery or a  
Ni-H battery, and the weight thereof is approximately half that of the Ni-Cd battery or the  
Ni-H battery. Thus, the lithium secondary battery is suitably used for small size,  
30 lightweight, longlasting electronic devices.

As described above, lithium secondary batteries have attracted particular attention because of their excellent characteristics, such as high operating voltage, much better charging/discharging cycle and environmentally benign characteristics and so on, compared to conventional Ni-Cd batteries or Ni-H batteries. However, since they are highly explosive, safety is a critical issue for practical use of lithium secondary batteries.

Lithium secondary batteries are classified according to the kind of electrolyte used, into lithium ion batteries using liquid electrolyte and lithium ion polymer batteries using polymer solid electrolyte.

The lithium ion battery generally utilizes a cylindrical case or a rectangular case as a case for hermetically sealing the electrode assembly. However, recently, a greater attention has been paid to a method in which a pouch is used instead of the case because use of the pouch increases energy density per unit weight or volume and allows attainment of small, lightweight batteries at low cost.

FIG. 1 is an exploded perspective view of an exemplary lithium ion battery using a pouch as a case.

Referring to FIG. 1, a lithium ion battery includes an electrode assembly 10 consisting of a cathode 11, an anode 12 and a separator 13, and a case 20 for hermetically sealing the electrode assembly 10. Here, the electrode assembly 10 is formed by interposing the separator 13 between the cathode 11 and the anode 12 and winding the structure. A cathode tap 11' and an anode tap 12' serving as electrical paths between the electrode assembly 10 and the exterior, are drawn from the cathode 11 and the anode 12 to form electrode terminals 14 and 14'.

FIG. 2 is an exploded perspective view illustrating an exemplary conventional lithium ion polymer battery.

Referring to FIG. 2, a lithium ion polymer battery includes an electrode assembly 21 having a cathode, an anode and a separator, and a case 22 for hermetically sealing the electrode assembly 21. Electrode terminals (or lead wires) 24 and 24' serving as electrical paths for inducing the current formed at the electrode assembly 21 to the

exterior are installed to be connected to a cathode tap 23 and an anode tap 23' to then be exposed by a predetermined length outside the case 22.

As described above, in the lithium ion battery shown in FIG. 1 and the lithium ion polymer battery shown in FIG. 2, the electrode assemblies 10 and 21 are put into the cases 20 and 22 and an electrolyte solution is inserted thereinto, with only parts of the electrode terminals 14 and 14' and 24 and 24' being exposed to the exterior. Then, heat and pressure are applied to each resultant structure so that thermally adhesive materials at the edges of the upper and lower case parts cause the upper and lower case parts to adhere together to then be hermetically sealed, thereby completing the batteries.

As described above, the electrolyte solution is injected in the latter part of the processing steps. Thus, in the case of using an organic solvent having a low boiling point, the electrode assemblies or pouches may be swollen, which deteriorates the battery reliability and safety.

To solve the problem, there have been proposed several methods, in which an electrode and an electrolyte are formed by hardening using ultraviolet rays or electron beams, or a gel-state electrolyte solution is coated on electrode plates without separate injection of an electrolyte solution, as disclosed in U.S. Patent Nos. 5,972,539, 5,279,910, 5,437,942 and 5,340,368. In practical application of the proposed methods, swelling of an electrode assembly or a pouch is somewhat mitigated, but is still not satisfactory.

#### [Technical Goal of the Invention]

To solve the above problems, it is an object of the present invention to provide a lithium secondary battery in which swelling due to an electrolyte solution is effectively suppressed so that reliability and safety do not degrade.

#### [Structure and Operation of the Invention]

According to an aspect of the present invention, there is provided a lithium battery including an electrode assembly consisting of a cathode, an anode and a separator interposed between the cathode and the anode, a gel-state electrolyte solution consisting of a crosslinking product of prepolymer for forming epoxy resin and amine, a lithium salt and an organic solvent, and a case for accommodating the electrode assembly and the electrolyte solution.

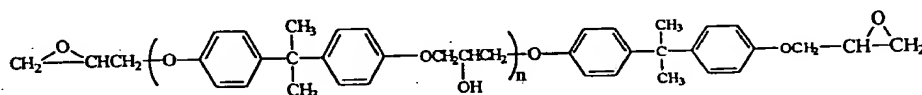
The electrolyte solution may be obtained by mixing the mixture of prepolymer for forming epoxy resin and amine with a mixture of the lithium salt and the organic solvent, injecting the resultant mixture into the case having the electrode assembly, and thermally polymerizing the same.

In particular, the electrode assembly is preferably of a winding type, and the case is preferably in the form of a pouch. Thus, the energy density of the battery per unit weight and volume is increased. Also, attainment of a small size and light weight battery is allowed. Further, the cost of a raw material for the case can be reduced.

The feature of the present invention lies in that, instead of a conventional liquid-phase electrolyte solution, a gel-state electrolyte solution consisting of a crosslinking product of prepolymer for forming epoxy resin and amine, a lithium salt, and an organic solvent.

The prepolymer for forming epoxy resin is a compound containing two or more epoxide rings, represented by formula 1:

[Formula 1]



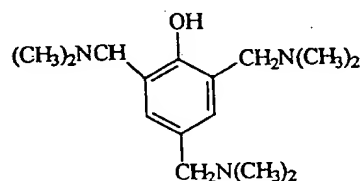
wherein n is an integer from 2 to 100.

The weight-average molecular weight of the compound represented by formula 1 is preferably 1000 to 3000. If the weight-average molecular weight of the compound

represented by formula 1 is outside the above-noted range, the compound is undesirably difficult to dissolve.

The amine is not specifically restricted, but a compound having two or more tertiary amine groups represented by formula 2 is preferably used. Here, use of the tertiary amine groups represented by formula 2 facilitates suppression of a side reaction of the crosslinking reaction between prepolymer for forming epoxy resin and amine.

[Formula 2]



A process for preparing a gel-state electrolyte solution using prepolymer for forming epoxy resin and amine will now be described.

First, prepolymer for forming epoxy resin and amine are mixed in an appropriate molar ratio and then added to a lithium salt and an inorganic solvent to then be mixed. Here, the molar ratio of prepolymer for forming epoxy resin to amine is preferably in the range of 1:1 to 5:1. If the molar ratio of prepolymer for forming epoxy resin to amine is outside the above-stated range, gelation is not easily achieved. During the mixing step, the ratio of the total weight of prepolymer for forming epoxy resin and amine to the total weight of the lithium salt and the inorganic solvent is preferably in the range of 1:1 to 1:20. Here, if the ratio of the total weight of prepolymer for forming epoxy resin and amine to the total weight of the lithium salt and the inorganic solvent is greater than the above range, gelation is not easily achieved. If the ratio of the total weight of prepolymer for forming epoxy resin and amine to the total weight of the lithium salt and the inorganic solvent is less than the above range, the performance of a battery is undesirably deteriorated.

Next, the mixture is thermally polymerized at a temperature in the range of 70 to 200°C. Then, the crosslinking reaction between prepolymer for forming epoxy resin

and amine occurs and then a crosslinking product thereof is prepared, so that gelation of the electrolyte solution is achieved.

In the present invention, usable organic solvents forming the electrolyte solution include at least one carbonate based solvent selected from the group consisting of propylene carbonate (PC), ethylene carbonate (EC), dimethylcarbonate (DMC), methylethyl carbonate (MEC), diethylcarbonate (DEC) and vinylene carbonate (VC). In particular, in the case of using vinylene carbonate (VC) as the organic solvent of the electrolyte solution, the performance of a battery, specifically, a lifetime characteristic, is improved. Usable lithium salts include at least one ionic lithium salt selected from the group consisting of lithium perchlorate ( $\text{LiClO}_4$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), lithium hexafluorophosphate ( $\text{LiPF}_6$ ), lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) and lithium bistrifluoromethanesulfonyl amide ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ).

A method for preparing a lithium battery according to the present invention containing the above-described electrolyte solution will now be described.

First, an electrode active material layer is formed on a current collector using an electrode active material composition containing an electrode active material, a binder, a conductive agent and a solvent. Here, the method for forming the electrode active material layer includes a method in which the electrode active material composition is directly coated on the current collector. Alternatively, the electrode active material coated on a separate support body and dried, and then a film obtained by being peeled off from the support body is laminated on the current collector. Here, any material that is capable of supporting an electrode active material layer can be used as the support body, and detailed examples thereof include a mylar film, a polyethyleneterephthalate (PET) film and the like.

In the present invention, lithium composite oxide such as  $\text{LiCoO}_2$ , or a sulfur compound such as active sulfur or organic sulfur is used as the cathode active material. Also, metallic lithium, carbon, graphite or the like, is used as the anode active material. Carbon black is used as the conductive agent. Here, the content of the conductive agent is preferably 1 to 20 parts by weight based on 100 parts by weight of the



electrode active material, e.g.,  $\text{LiCoO}_2$ . In particular, in the case of using metallic lithium as the anode active material, the safety of a battery can be greatly improved by using the electrolyte solution according to the present invention.

As the binder, at least one selected from the group consisting of  
5 polyvinylidene fluoride-hexafluoropropylene copolymer (VdF-HFP copolymer),  
polyvinylidene fluoride, polyacrylonitrile, polymethylmethacrylate and a mixture thereof,  
and the content thereof is preferably 5 to 30 parts by weight based on 100 parts by  
weight of the electrode active material.

Any solvent that is generally used for lithium batteries can be used as the solvent,  
10 and detailed examples thereof include acetone, N-methylpyrrolidone, and the like.

Occasionally,  $\text{Li}_2\text{CO}_3$  may be further added to the electrode active material  
composition. Adding  $\text{Li}_2\text{CO}_3$  enhances the battery performance, specifically, high-rate  
performance.

The separator used in the present invention is not specifically limited, and a  
15 polyethylene separator or a polypropylene separator that is easily wound is preferably  
used.

Then, the separator is interposed between the cathode plate and the anode plate  
and then wound in a jelly-roll type configuration to fabricate an electrode assembly (see  
FIG. 1) or a bi-cell electrode assembly (see FIG. 2). Subsequently, the electrode  
20 assembly is put into a case. Then, prepolymer for forming epoxy resin and amine are  
mixed in an appropriate molar ratio and then added to a lithium salt and an inorganic  
solvent to then be mixed. The mixture is injected into the case.

Thereafter, the case is hermetically sealed and then the resultant structure is  
allowed to stand at an oven maintained at a predetermined temperature for a  
25 predetermined time. The temperature of the oven is preferably adjusted to be in the  
range of 70 to 200°C. If the temperature of the oven is lower than 70°C,  
polymerization does not occur. If the temperature of the oven is higher than 200°C,  
the binder is undesirably dissolved.

As the result of the reaction, thermal polymerization between prepolymer for forming epoxy resin and amine occur to produce a crosslinking product, so that the electrolyte solution is turned into a gel phase. As described above, if the electrolyte solution exists in the gel-state, it is not likely to be leaked outside. Also, swelling of an electrode assembly or a pouch due to the electrolyte solution can be prevented. Further, the safety or reliability of the battery can be prevented from lowering due to leakage of the electrolyte solution.

The present invention will now be described with reference to the following examples and is not limited thereto.

#### Example 1

15 g of polyvinylidenefluoride was added to 600 ml of acetone and mixed at a ball mill for 2 hours to be dissolved. To the mixture were added 470 g of  $\text{LiCoO}_2$  and 15 g of Super P. and then mixed for 5 hours to form a cathode active material composition.

The cathode active material composition was coated on an aluminum film having a thickness of 147  $\mu\text{m}$  and a width of 4.9 cm using a doctor blade having a gap of 320  $\mu\text{m}$  and dried to form a unit cathode plate.

Next, the anode plate was fabricated as follows.

50 g of polyvinylidenefluoride was added to 600 ml of acetone and mixed at a ball mill for 2 hours to be dissolved. To the mixture were added 449 g of mezocarbon fiber (MCF) and 1 g of oxalic acid for increasing the adhesion to a copper film, and then mixed for 5 hours to form an anode active material composition.

The anode active material composition was coated on a copper film having a thickness of 178  $\mu\text{m}$  and a width of 5.1 cm using a doctor blade having a gap of 420  $\mu\text{m}$  and dried to form a unit anode plate.

Separately, a polyethylene separator manufactured by Asahi Kasei Kogyo Kabushiki Kaisha was used as a separator. Here the width of the separator was 5.25 cm and the thickness thereof was 18  $\mu\text{m}$ .

The polyethylene separator was interposed between the cathode plate and the anode plate and then wound in a jelly-roll type configuration to fabricate an electrode assembly. The fabricated electrode assembly was put into a pouch.

Then, 3 g of prepolymer for forming epoxy resin, represented by formula 1,  
5 having a molecular weight of 2000, and 1 g of amine represented by formula 2, was mixed with 12 g of 1M LiPF<sub>6</sub> dissolved in a mixture solvent containing propylene carbonate (PC) and ethylene carbonate (EC) in the ratio by volume of 1:1. 6 g of the obtained mixture was injected into the pouch battery obtained in the above-described manner and then hermetically sealed. Then, the resultant structure was allowed to  
10 stand in an oven maintained at 85° for 2 hours, thereby completing a lithium secondary battery.

#### Example 2

In the step of mixing the mixture of 3 g of prepolymer for forming epoxy resin represented by formula 1 and 1 g of amine represented by formula 2 with 12 g of 1M  
15 LiPF<sub>6</sub> dissolved in a mixture solvent containing PC and EC in the ratio by volume of 1:1, a lithium secondary battery was completed in the same manner as in Example 1, with the exception of 1M LiPF<sub>6</sub> dissolved in a mixture solvent containing PC, EC and vinylene carbonate (VC) in the ratio by volume of 4:4:2 being used, instead of 1M LiPF<sub>6</sub> dissolved in a mixture solvent containing PC and EC in the ratio by volume of 1:1.

#### Example 3

A lithium secondary battery was completed in the same manner as in Example 1, with the exception of 3 g of prepolymer for forming epoxy resin represented by formula 1 and 2 g of amine represented by formula 2 being used.

#### Example 4

25 A lithium secondary battery was completed in the same manner as in Example 1, with the exception of 1 g of Li<sub>2</sub>CO<sub>3</sub> being further added in the course of preparing the cathode active material composition and the anode active material composition.

#### Comparative Example

A lithium secondary battery was completed in the same manner as in Example 1, with the exception of 1.15M  $\text{LiPF}_6$  dissolved in a mixture solvent of EC, dimethyl carbonate (DMC), and diethyl carbonate (DEC) in the ratio by volume of 3:3:4, being used as the electrolyte solution.

5        The charge/discharge characteristics of the lithium secondary batteries manufactured in Examples 1 through 4 and Comparative Example were evaluated. The reliability of a battery was evaluated by examining the extent of swelling after the battery was allowed to stand at 80°C for 3 days. The safety of a battery was evaluated by carrying out overcharging piercing and overcharging tests.

10        The evaluation results show that the lithium secondary batteries manufactured in Examples 1 through 4 had excellent reliability and safety compared to the lithium secondary battery manufactured in Comparative Example. This is because the lithium secondary batteries manufactured in Examples 1 through 4 used gel-state electrolyte solutions so that the electrolyte solutions seldom leak outside, unlike the lithium  
15        secondary battery manufactured in Comparative Example using a liquid-phase electrolyte solution. Also, swelling of an electrode assembly or a pouch due to an electrolyte solution can be prevented. Thus, it is unlikely that the reliability and safety of the lithium secondary batteries manufactured in Examples 1 through 4 deteriorate.

20        In the cases of further adding vinylene carbonate as an organic solvent forming the electrolyte solution as in Example 2 and further adding  $\text{Li}_2\text{CO}_3$  in the course of preparing the cathode active material composition and the anode active material composition as in Example 4, it was confirmed that the lifetime characteristic was particularly superior.

25        [Effect of the Invention]

According to the present invention, swelling due to an electrolyte solution can be effectively suppressed and the electrolyte solution does not leak. Accordingly, a lithium secondary battery that has no concern about degradations in reliability and safety can be attained.

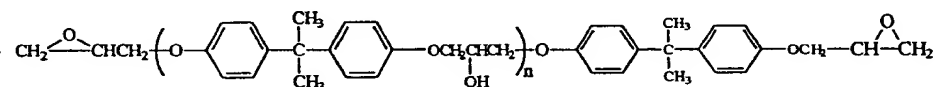
Although the present invention has been described with reference to the preferred examples, the foregoing disclosure should be interpreted as illustrative only and it should be understood that various modifications and variations can be easily made by those skilled in the art without departing from the spirit of the invention.

- 5 Accordingly, a true scope and spirit of the invention should be defined by the following claims.

What is claimed is:

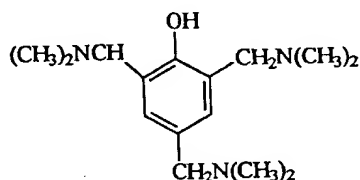
1. A lithium secondary battery comprising:  
an electrode assembly consisting of a cathode, an anode and a separator  
interposed between the cathode and the anode;  
5 a gel-state electrolyte solution consisting of a crosslinking product of prepolymer  
for forming epoxy resin and amine, a lithium salt and an organic solvent; and  
a case for accommodating the electrode assembly and the electrolyte solution.

2. The lithium secondary battery according to claim 1, wherein the  
10 prepolymer for forming epoxy resin is a compound represented by formula 1:



15 wherein  $n$  is an integer of 2 through 100.

3. The lithium secondary battery according to claim 1, wherein the amine is  
represented by formula 2:



25 4. The lithium secondary battery according to claim 1, wherein the molar  
ratio of prepolymer for forming epoxy resin to amine is in the range of 1:1 to 5:1.

5. The lithium secondary battery according to claim 1, wherein the ratio of the total weight of prepolymer for forming epoxy resin and amine to the total weight of the lithium salt and the organic solvent is in the range of 1:1 to 1:20.

5 6. The lithium secondary battery according to claim 1, wherein the electrolyte solution is obtained by mixing the mixture of prepolymer for forming epoxy resin and amine with a mixture of the lithium salt and the organic solvent, injecting the resultant mixture into the case having the electrode assembly, and thermally polymerizing the same.

10 7. The lithium secondary battery according to claim 6, wherein the thermal polymerization temperature is in the range of 70 to 200°C.

15 8. The lithium secondary battery according to claim 1, wherein the lithium salt is at least one selected from the group consisting of lithium perchlorate ( $\text{LiClO}_4$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), lithium hexafluorophosphate ( $\text{LiPF}_6$ ), lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) and lithium bistrifluoromethanesulfonyl amide ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ), and the organic solvent is at least one carbonate based solvent selected from the group consisting of propylene carbonate (PC), ethylene carbonate  
20 (EC), dimethylcarbonate (DMC), methylethyl carbonate (MEC), diethylcarbonate (DEC) and vinylene carbonate (VC).

9. The lithium secondary battery according to claim 1, wherein the electrode assembly is of a winding type, and the case is in the form of a pouch.

FIG. 1

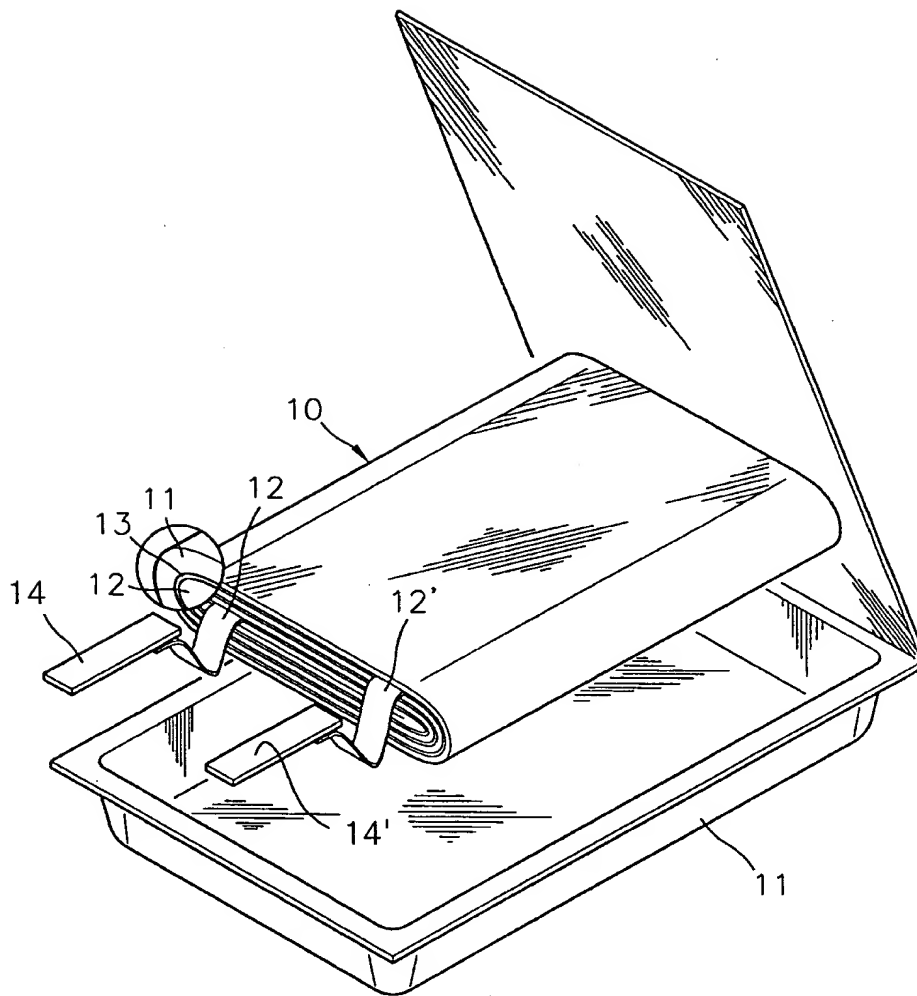




FIG. 2

